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STANDARD METHODS

FOR THE EXAMINATION OF WATER AND WASTEWATER

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3500-Cd CADMIUM*

3500-Cd A. Introduction

1. Occurrence and Significance

Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. Cadmium also causes generalized cancers in laboratory animals and has been linked epidemiologically with certain human cancers. A cadmium concentration of 200 μg/L is toxic to certain fish. Cadmium may enter water as a result of industrial discharges or the deterioration of galvanized pipe.

2. Selection of Method

The electrothermal (graphite furnace) atomic absorption spectrometric method is preferred. The flame atomic absorption and inductively coupled plasma methods provide acceptable precision and bias, with higher detection limits. The dithizone method is suitable when atomic absorption spectrometric or inductively coupled plasma apparatus is unavailable and the desired precision is not as great.

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*Approved by Standard Methods Committee, 1990.

3500-Cd B. Atomic Absorption Spectrometric Method

See flame atomic absorption spectrometric method, Sections 3111B and C, and electrothermal atomic absorption spectrometric method, Section 3113.

3500-Cd C. Inductively Coupled Plasma Method

See Section 3120.

3500-Cd D. Dithizone Method

1. General Discussion

a. Principle: Cadmium ions under suitable conditions react with dithizone to form a pink to red color that can be extracted with chloroform ($CHCl_3$). Chloroform extracts are measured photometrically and the cadmium concentration is obtained from a calibration curve prepared from a standard cadmium solution treated in the same manner as the sample.

b. Interference: Under the specified conditions, concentrations of metal ions normally found in water do not interfere. Lead up to 6 mg, zinc up to 3 mg, and copper up to 1 mg in the portion analyzed do not interfere. Ordinary room lighting (incandescent or fluorescent) does not affect the cadmium dithizonate color.

c. Minimum detectable concentration: 0.5 μg Cd in approximately 15 mL final volume with a 2-cm light path.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 518 nm with a minimum light path of 1 cm.

2) *Filter photometer,* equipped with a green filter having a maximum light transmittance near 518 nm, with a minimum light path of 1 cm.

b. Separatory funnels, 125-mL, preferably with TFE stopcocks.

c. Glassware: Clean all glassware, including sample bottles, with 1 + 1 HCl and rinse thoroughly with tap water and distilled water.

3. Reagents

a. Water, cadmium-free: Redistill distilled water in an all-glass still. Use this water to prepare all reagents and solutions.

b. Stock cadmium solution: Weigh 100.0 mg pure Cd metal and dissolve in a solution composed of 20 mL water plus 5 mL conc HCl. Use heat to assist metal dissolution. Transfer quantitatively to a 1-L volumetric flask and dilute to 1000 mL; 1.00 mL = 100 μg Cd. Store in a polyethylene container.

c. Standard cadmium solution: Pipet 1.00 mL stock cadmium solution into a 100-mL volumetric flask, add 1 mL conc HCl, and dilute to 100 mL with water. Prepare as needed and use the same day; 1.00 mL = 1.00 μg Cd.

d. Sodium potassium tartrate solution: Dissolve 250 g $NaKC_4H_4O_6 \cdot 4H_2O$ in water and make up to 1 L.

e. Sodium hydroxide-potassium cyanide solutions:

1) *Solution I:* Dissolve 400 g NaOH and 10 g KCN in water and make up to 1 L. Store in a polyethylene bottle. This solution is stable for 1 month.

2) *Solution II:* Dissolve 400 g NaOH and 0.5 g KCN in water and make up to 1 L. Store in a polyethylene bottle. This solution is stable for 1 to 2 months.

CAUTION—*Potassium cyanide is extremely poisonous. Be especially cautious when handling it. Never use mouth pipets to deliver cyanide solutions.*

f. Hydroxylamine hydrochloride solution: Dissolve 20 g $NH_2OH \cdot HCl$ in water and make up to 100 mL.

g. Stock dithizone solution I: See Section 1070D.2*b*1).

h. Working dithizone solution: Dilute stock dithizone solution I with $CHCl_3$ to produce a working solution of 10 µg/mL. Prepare daily.

i. Chloroform, ACS grade passed for "suitability for use in dithizone test." Test for a satisfactory $CHCl_3$ by adding a minute amount of dithizone to a portion of the $CHCl_3$ in a stoppered test tube so that a faint green is produced; the green color should be stable for a day.

j. Tartaric acid solution: Dissolve 20 g $H_2C_4H_4O_6$ in water and make up to 1 L. Store in refrigerator and use while still cold.

k. Hydrochloric acid, HCl, conc.

l. Thymol blue indicator solution: Dissolve 0.4 g thymolsulfonephthalein sodium salt in 100 mL water.

m. Sodium hydroxide, NaOH, 6*N*.

4. Procedure

a. Preparation of standard curve: Prepare a blank and a series of standards from 1 to 10 µg by pipetting the appropriate amounts of standard Cd solution into separatory funnels. Dilute to 25 mL and proceed as in ¶ 4*c*. Plot a calibration curve.

b. Treatment of samples: Digest sample as directed in Section 3030. Pipet a volume of digested sample containing 1 to 10 µg Cd to a separatory funnel and dilute to 25 mL as necessary. Add 3 drops thymol blue and adjust with 6*N* NaOH to the first permanent yellow color, pH 2.8.

c. Color development, extraction, and measurement: Add reagents in the following order, mixing after each addition: 1 mL sodium potassium tartrate solution, 5 mL NaOH-KCN solution I, 1 mL $NH_2OH \cdot HCl$ solution, and 15 mL stock dithizone solution I. Stopper funnels and shake for 1 min, relieving vapor pressure in the funnels through the stopper rather than the stopcock. Drain $CHCl_3$ layer into a second funnel containing 25 mL cold tartaric acid solution. Add 10 mL $CHCl_3$ to first funnel; shake for 1 min and drain into second funnel. Do not permit aqueous layer to enter second funnel. Because time of contact of $CHCl_3$ with the strong alkali must be kept to a minimum, make the two extractions immediately after adding dithizone (cadmium dithizonate decomposes on prolonged contact with strong alkali saturated with $CHCl_3$).

Shake second funnel for 2 min and discard $CHCl_3$ layer. Add 5 mL $CHCl_3$, shake 1 min, and discard $CHCl_3$ layer, making as close a separation as possible. In the following order, add 0.25 mL $NH_2OH \cdot HCl$ solution and 15.0 mL working dithizone solution. Add 5 mL NaOH-KCN solution II; *immediately* shake for 1 min and transfer $CHCl_3$ layer into a dry photometer tube. Read absorbance at 518 nm against the blank. Obtain Cd concentration from calibration curve.

5. Calculation

$$\text{mg Cd/L} = \frac{\mu\text{g Cd (in approx. 15 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 50 µg Cd/L, 500 µg Al/L, 110 µg Cr/L, 470 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 150 µg Ag/L, and 650 µg Zn/L was analyzed in 44 laboratories by the dithizone method with a relative standard deviation of 24.6% and a relative error of 6.0%.

7. Bibliography

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